PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Masayoshi TAKAHASHI, et al.

Appln. No.: 10/790,716

Confirmation No.: 2616

Filed: March 3, 2004

Docket No: Q79574

Group Art Unit: 1797

Examiner: John Christopher DOUGLAS

For: MANUFACTURING GAS HYDRATE USING MICROBUBBLE

DECLARATION UNDER 37 C.F.R. § 1.132

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Masayoshi TAKAHASHI, hereby declare and state:

THAT I am a citizen of Japan;

THAT I have received the degree of Ph.D. in Engineering from Kyushu University;

THAT I have been employed by National Institute of Advanced Industrial Science and Technology (Formerly named as Agency of Industrial Science and Technology) since 1985, where I hold a position as Senior Research Scientist, with responsibility for;

I have reviewed the references cited by the Examiner in the pending Office Action in the above case.

I believe that the Examiner is mischaracterizing the teachings of the references Arai, Ida and Kato. Based on my experience, gas bubbles smaller than 50 μm are not formed in any of the

three references and there is no basis for concluding that gas hydrates will be generated by self-compression in any of the three references.

The Arai reference

In Arai's technology, forming a water flow downward to counter the gas bubbles rising upwards is a key point. Paragraph [0028] of Arai reference (JP 2003-041275A) discloses that a preferable flow-down speed of water in generation tub may be in the range of 0.1 to 3 m/s. Since Arai tries to keep bubbles in the system longer, rising speed of bubbles in Arai technology must be comparable to the flow-down speed of water. In other words, bubbles in Arai must flow-up at a speed of 0.1 to 3 m/s. It is known that rising speed of micro bubbles in water nearly obeys Henry's Law. Diameters of bubbles in Arai's technology can be calculated and found somewhere around 0.56mm (560μm) to 3.1 mm (3100μm).

Figure A

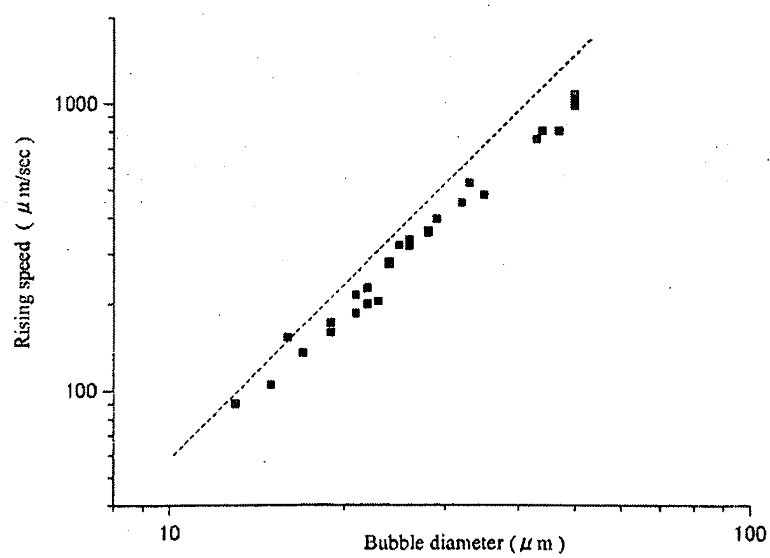
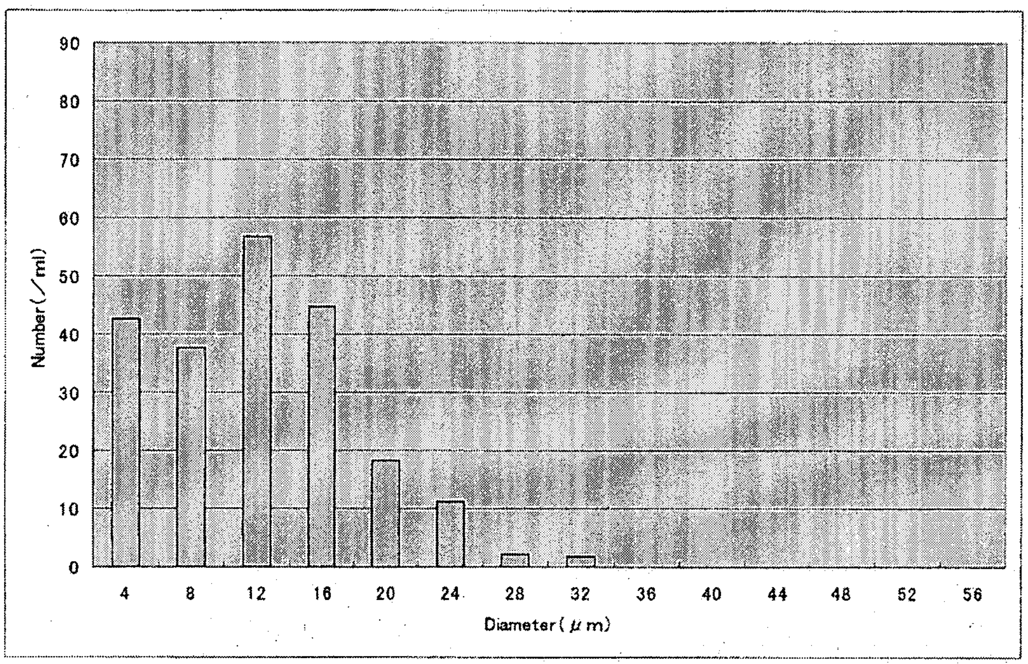


Figure A, shown above, shows the relation between bubble diameters, which are 50 μm or less, and their rising speeds in water. This Figure is, actually, a reproduction from my paper (J. Phys. Chem. B 109, pp21858-21864). As easily be seen in the Figure A, rising speeds of bubbles with a diameter of 50 μm and 10 μm are about 0.001 m/s and 0.00006 m/s, respectively.

It is, therefore, undisputable that sizes of bubbles in Arai are significantly bigger than that in the present invention. In addition, if the technology described in Arai technology is applied to a system containing bubbles with diameters of 50 μm or less, such micro bubbles would be dispelled from the system easily by the downward current of water.

Figure B, shown below, shows a particle diameter distribution of hydrates produced in an experiment which is in line with the present invention. Counting particles of hydrates was performed with a particle counter for liquid media (LiQuilaz-E20, manufactured by Particle Measuring Systems, Inc.). Figure B reveals that almost all gas hydrates have diameters of 30 μm or less.

Figure B



On the other hand, diameters of gas hydrates produced in a conventional method are more than 0.1 mm (100μm).

Clearly Arai aims to increase contact time of gas bubbles with a water flow counter the rising gas bubbles to attain more efficient production of hydrates. Paragraph [0029] of the Arai reference explains that by lengthening holding time of bubbles in a generation tub, growth time of gas hydrate is lengthened, and accordingly the hydrates having larger diameters may be produced. Apparently, Arai deals with bubbles having incomparably bigger diameter than in the present invention. Therefore, it does not suggest bubbles with diameter of 50 μm or less at all.

<u>The Ida reference:</u>

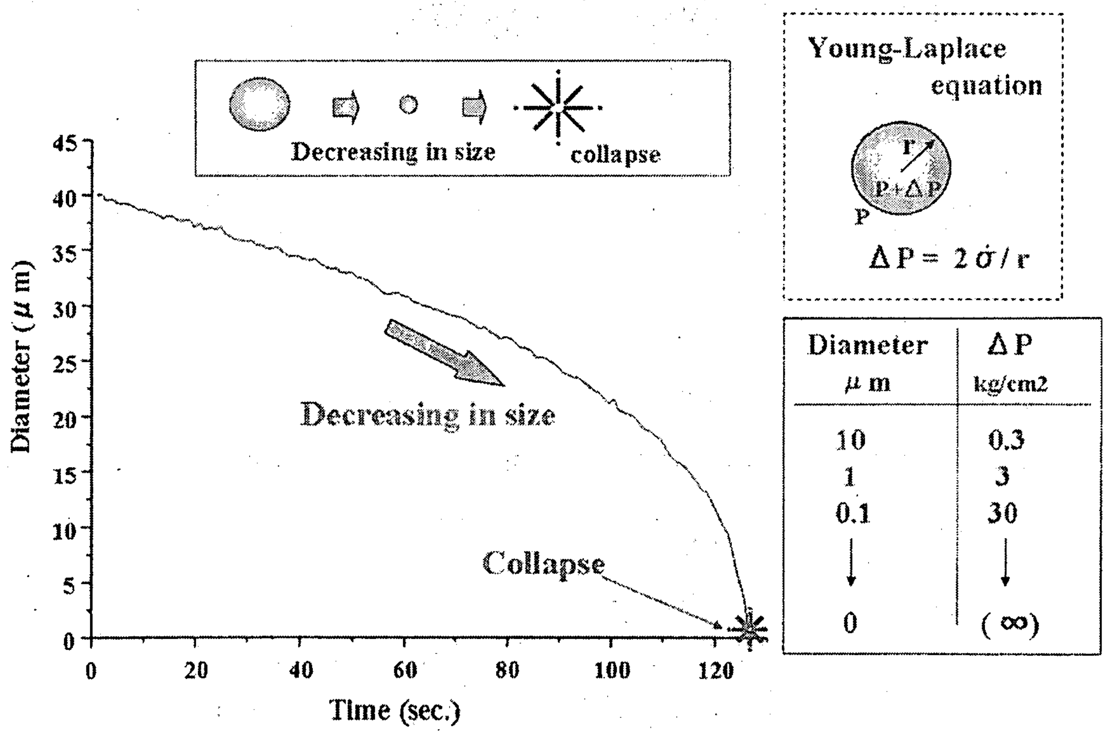
A key point in Ida's technology is to divide the production processes into three phases in order to make gas hydrate production more effectively. The three phases are – 1) micro bubble production phase, 2) gas dissolution phase, and 3) gas hydrate production phase.

In Ida, even if bubbles having diameters of 50μm or less were produced in the first phase (micro bubble production phase), such gas bubbles are to be dissolved into water in the next phase (gas dissolution phase). Therefore, Ida intends to have no bubbles in water in the third phase (gas hydrate production phase). Requirements in producing gas hydrate such as high pressure and a low temperature are attained in the third phase (gas hydrate production phase) for the first time in Ida. It is apparent that Ida does not satisfy the requirement of the present invention, i.e. bubbles with 50μm or less being present when high pressure and low temperature are attained in the gas hydrate production process.

Figure C, shown below, illustrates a graph showing a change of diameter of micro bubble with time. A micro bubble was put in a micro cell filled with water and the size of the micro bubble was observed with a microscope, and images with time were taken into a PC by image analysis method. When initial diameter of a bubble was 40μm, the bubble lasted for about 2 minutes. From the curvature of the graph in Figure C, we can see that a smaller bubble would shrink faster than a bigger one does. This is because that a relatively smaller bubble has a bigger inner pressure, which gives a greater gas-dissolution into water, than that of a relatively bigger bubble. From these, it would be expected that a bubble of 50μm in diameter would collapse in about three minutes.

It is impossible to complete all the processes Ida requires in three minutes. Since heat capacity of water is relatively big, it takes time to cool down water in the system, we would easily expect that in the third process of Ida, there would be no bubbles having 50μm or less left in the system.

Figure C



Diameter μ m	ΔP kg/cm2
10	0.3
1	3
0.1	30
↓	↓
0	(∞)

<u>**On Kato reference:**</u>

Kato (JP 2003-055677A) generally relates to generation of gas hydrate particles in different sizes by using porous plate having various sizes of pores. In Kato's method, as described in paragraph [0015], a big bubble in size will produce a big hydrate particle in

diameter, and a small size bubble for a small hydrate particle. Since gas-dissolved region surrounding a bubble in water engages in the production of hydrate, there is a correlation between size of bubbles and sizes of hydrate particles. Kato regulates bubble size in order to produce a certain size of hydrate particle. Paragraph [0036] of Kato reference discloses that a coarse hydrate particle in the experiment had a size of about 0.5 mm, and a fine particle had a size of about 0.25 mm. Since a produced hydrate is smaller in size than corresponding bubble, a bubble which produces a fine hydrate of about 0.25 mm in size would be greater than 0.25 mm. In sum, Kato uses bubbles of 250μm or greater in size.

It is impossible to produce bubbles having diameters of 50μm or less by using Kato's method, i.e. by using a perforated plate. There are limitations in producing micro bubbles even if we prepare small pores in the plate. For example, a pore having 1μm diameter would give a bubble of 100μm or greater in size at the time the bubble detaches from the pore portion of the plate because the bubble inflates like a toy balloon.

To confirm this, I performed an experiment by using a plate having pores, each of which having a diameter of 1μm in order to find how big in size of bubble can be produced with Kato's method. The particle counter mentioned above was used to find bubble sizes. It turned out that no measurable bubbles by the counter were found. That means that all the bubbles produced in the experiment were bigger than the measurable range (125μm or less) of the counter. If we make pores having diameters much smaller than 1μm, then we may find difficulty in producing bubbles into water because of the effect of surface tension of water. Therefore, it is impossible to produce bubbles having diameters of 50μm or less by Kato's method unless we introduce a

surfactant in water. However, surfactant prevents to some extent the dissolution of gas into water, resulting that bubbles have a longer life in water. Such would prevent obtaining a similar effect as in the present invention from Kato's method.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: February 3, 2009

高橋正好
Masayoshi TAKAHASHI